

Title: **Characterization of Process Samples from Co-Liquefaction of Coal and Waste Polymers**

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INTRODUCTION

Since 1994, CONSOL has characterized feed, recycle, and product samples from DOE-sponsored co liquefaction experiments with polymers and coal.¹⁻⁵ The objective is to understand the process chemistry and the fate of the polymer components in continuous unit runs. CONSOL used conventional liquefaction process stream characterization methods, supplemented by methods developed specifically for polymer components. In the earliest Hydrocarbon Technologies, Inc. (HTI) runs, virgin polymers were used to simulate municipal waste polymers. More recently, HTI began using authentic municipal solid waste polymers (Run CMSL-1⁶) and auto shredder residue (Run PB-04⁷) as co-liquefaction feedstocks in various combinations with coal petroleum resid, and virgin polymers. Process stream samples were characterized from HTI runs in which these authentic waste polymers were liquefied with coal and petroleum resid. The conversion of relatively unreactive polyolefins was determined by an extraction procedure. The fate of polystyrene was determined by gas chromatography-mass spectrometry of net liquid products.

BRIEF DESCRIPTION OF PLANT AND CO-LIQUEFACTION RUNS

The co-liquefaction runs were performed in HTI's bench unit 227. Fresh feed materials (catalyst precursors, coal, waste feedstocks, petroleum resid, and/or virgin polymers) were mixed batchwise with process recycle materials in a tank and transferred to a feed slurry tank that continuously fed the slurry to the liquefaction process. The feed slurry was fed to a preheater that also conditioned the dispersed catalyst. Next, the slurry was fed to two successive stages of liquefaction. No supported catalysts were used in the liquefaction reactors; only disposable dispersed catalysts were used. A high-pressure separator after the first reactor allows light products to be taken off, and the hydrogen concentration to be increased in the second reactor. The first-stage oil, called the first-stage separator overhead oil, or SOH1, is sent with second-stage light oils and light distillate to an in-line fixed-bed hydrotreater. The in-line hydrotreater upgrades the product using the liquefaction reactor system off gases. The second stage of liquefaction is followed by high- and low pressure separators. The separator overheads are fed to the in-line product hydrotreater, and the separator bottoms to distillation. The distillate (ca. IBP-371 °C) is sent to the product hydrotreater, and the resid is filtered to provide a liquid for recycle and solids to reject ash. Major streams analyzed typically included the feed slurry, individual fresh feeds, the unhydrotreated first-stage separator overhead (SOH1) oil, the separator bottoms (flashed liquefaction product), the filter liquid (recycle), filter cake (solids), and the hydrotreated net product oil.

Operating conditions for relevant portions of Runs CMSL-1⁶ and PB-04⁷ are shown in Table 1. In both runs, co-liquefaction operation was successfully demonstrated using the municipal or industrial waste feedstocks (municipal solid waste (MSW) plastics in Run CMSL-11, and automobile shredder residue (ASR) in Run PB-04). When MSW was fed with coal, Condition 3B of Run CMSL-11, H₂ consumption and gas yield were reduced and distillate yield increased. In general, ASR was not as beneficial as MSW to liquefaction process

performance. Operating difficulties were encountered throughout the ASR run. HTI observed that: 1) ASR caused repeated feed pump problems; 2) the resid conversion was lower when ASR was fed (relative feeding coal only); and 3) ASR lowered the H consumption, distillate yield, and light gas yield. HTI speculated that polyurethane and (cross-linked) high impact polystyrene in the ASR were less reactive than polymers previously processed (including the MSW). It is important to determine the relative reactivity of the polymers that could be identified in the ASR.

Table 1. Conditions and Yields for HTI Runs PB-04 (227-95) and CMSL-11 (227-89)

Run	PB-04					CMSL-11	
Condition	1	2	3	4	5	2	3B
Feed, wt % MF							
Black Thunder Coal	100	-	50	75	50	100	75
Hondo resid	-	70	30	-	-	-	-
ASR (PB-04) or MSW (CMSL-11)	-	30	20	25	25	-	25
HDPE/PS (60:40)	-	-	-	-	25	-	-
Temp. Stage 1/Stage 2, °C	440/450					450/460	
Disp. Cat. Loading, mg/kg	Fe :1000, Mo:50, P:100					Fe:5000, Mo:100	
Yields, wt % MAF Fresh Feed							
C ₁ -C ₃ Gases	9.9	7.0	8.6	6.9	7.8	18.2	7.4
C ₄ -343 °C	46.0	44.4	48.3	31.2	40.3	49.4	39.5
343-524 °C	21.6	24.7	18.5	25.4	21.2	13.5	28.1
524 °C+	3.7	16.0	10.5	18.0	14.0	6.0	11.2
Unconverted Feed	6.8	3.6	6.0	9.6	8.8	4.9	5.3
H ₂ O+COx	18.6	5.0	11.6	15.2	12.1	14.5	13.6
NH ₃ +H ₂ S	0.6	4.2	2.3	-0.3	-0.8	0.4	-0.2
H ₂ Consumption	7.2	4.8	5.7	6.0	4.0	6.9	4.9
MAF Feed Conv., wt % (SO ₃ -Free)	93.2	96.4	94.1	90.5	91.3	95.1	94.7

DESCRIPTION OF CHARACTERIZATION METHODS

Three analytical techniques supplemented the normal liquefaction work-up procedures (which usually include distillation, tetrahydrofuran (THF) extraction, ashing, and determinations of phenolic -OH concentration and proton distribution). When polymers are present in co-liquefaction samples, hot decalin extraction, FTIR spectroscopy, and GC-MS characterization are the supplementary techniques. The decalin extraction and FTIR are used typically for resid- and solids-containing samples, and GC-MS is used typically for light net product oils. The hot decalin extraction method was described previously⁵; it generates a solubles fraction, a "plastic" fraction, and an insolubles fraction from a liquefaction sample. The "plastic" fraction consists of polyolefins (primarily high-density polyethylene (HDPE) and polypropylene (PP)) that are soluble in hot decalin, but insoluble in THF or room-temperature decalin. The polymers are subsequently characterized by FTIR spectroscopy. The GC-MS total ion chromatograms and individual mass spectra are usually examined for information on n-paraffins from polyethylene and other feedstocks, and for marker compounds from polystyrene (PS) liquefaction. Various sample preparation techniques have been used at CONSOL for qualitative FTIR examination of polymeric materials. Unsupported and supported thin films and thin slices have been used for transmission IR measurements. Powder, or fine cuttings or filings have been mixed with KBr (1-10% polymer) for diffuse reflectance measurements.

CHARACTERISTICS OF PROCESS STREAMS SAMPLES

Table 2 is a summary of the overall characterization results of the various process streams analyzed

components found or expected, and methods used. Ash, polyethylene, polypropylene, and polystyrene were components of the MSW and ASR feedstocks that were directly or indirectly identified. PS was identified via marker PS-derived compounds found in product oils using GC-MS. Ash was determined directly on the MSW and indirectly on the ASR, using the ash content of the feed slurry. A polyolefin component was extracted from the feed slurry samples, and identified as HDPE and PP using FTIR spectroscopy. Spectroscopic features suggest the presence of low-density polyethylene (LDPE), or some unidentified polyethylene, in some samples. Based on combined results from several of these methods, overall composition of the MSW feed is approximately 96% HDPE+PP, 2% PS, and 1.6% ash. Using the same procedure, the estimated composition of the ASR feed was 68% HDPE+PP, 12% PS, and 20% ash (as reported by HT).

Table 2. Components Found in Process Stream Samples From Co-Liquefaction of Waste Polymers With Coal

Stream Sample from Process	Component						Methods
	HDPE	PP	LDPE or Other PE	PS	Ash	Other Polymers	
Feed MSW	X	X		I	X	E	DE, FTIR
Feed ASR	I	I		I	X	E	
MSW Feed Slurry	X	X		I	X	E	DE, FTIR
ASR Feed Slurry	X	X	S	I	X	E	DE, FTIR
Separator Bottoms	X	C*			X		DE, FTIR
Filter Liquid	X	C*	S*				DE, FTIR
Filter Solids	X	C*	S*		X		DE, FTIR
First Stage Oil*	P	E		P			GC-MS
Product Oil	P	E		P			GC-MS
Legend: X = Direct evidence I = Indirect evidence P = Evidence for a product E = Expected, but not identified S = Suspected, i.d. uncertain C = Contrary evidence (i.e., that it is not present) DE = Hot decalin extraction							

* Applies to Run PB-04 samples only.

FATE OF HDPE AND PP

Previous work demonstrated that polyolefins, primarily HDPE and PP, could be extracted from co-liquefaction stream samples. The amount of this material rejected from the process represents the amount that is not converted to liquid products. FTIR spectroscopy (Figure 1) was used to identify PP and HDPE in polyolefin material extracted from feed slurries from Run PB-04. These results indicate that PP was a significant component of the feed ASR. The material extracted from the pressure-filter cake stream that is used to reject solids from the process consists entirely of polyethylene (Figure 1, apparently HDPE). This indicates that the PP is more reactive than the HDPE at reaction conditions.

Table 3 presents the ash-balanced, overall conversions of the total MAF feed, the total MAF waste/polymer feed, and the decalin-extracted polyolefins. The overall conversion is calculated from the compositions and flow rates of the net product and fresh feeds. However, decalin-extracted polyolefins were determined on the (Run PB-04) feed slurry samples, since no ASR sample was available. The recycled ash and polyolefins contributions were backed out to determine the relative concentrations of fresh polyolefins and ash. In turn, this allowed the percentage polyolefins in the ASR to be estimated at 79-90% MAF, or 63-72% (average of 68%) MF.

The CONSOL MAF fresh feed conversion is compared with HTI results in Table 3 to demonstrate that the ash balance technique typically gives conversions very similar to those of HTI. The exception in these data are the results for Conditions 4 and 5, for which the CONSOL conversions were ~3-5% lower than those obtained by HTI, possibly due to the difference between the solvents used. CONSOL used THF to define conversion (THF does not dissolve the unconverted polyolefins). HTI used hot quinoline to define conversion (hot quinoline does dissolve the unconverted polyolefins). The same ash balance method was used to calculate conversions of the total wastes and the decalin-extracted polyolefins. The results indicate high conversion of the total waste/polymer stream and of the polyolefins, ~95-99%. The conversions of these components were typically about 5% higher than HTI's conversions of the total fresh feed. The lower conversions observed by CONSOL for the total waste/polymer component and for the decalin-extracted polyolefins corresponded to Conditions 4 and 5 of Run PB-04, in which HTI also observed the lowest fresh feed conversions. Recycle of unconverted polyolefins (apparently chiefly HDPE) is required to achieve these high conversions. Evidently, conditions used in Conditions 4 and 5 of Run PB-04 were not optimal to convert all of the ASR or polyolefin component of the ASR. In Run CMSL-11, HTI used higher reactor temperatures, higher Mo and Fe catalyst concentrations (and different catalyst precursors) to achieve high conversion of the MSW polymers.

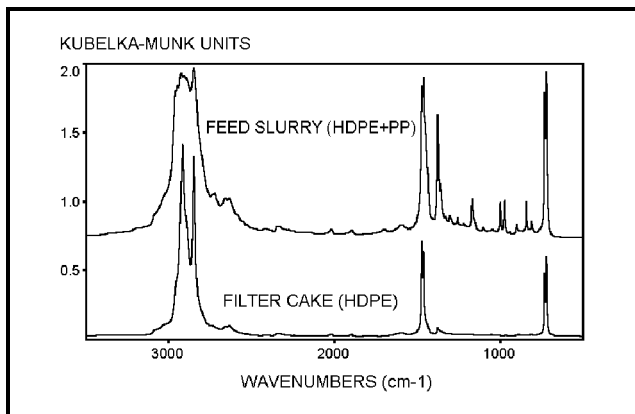


Figure 1. FTIR Spectra of Decalin-Extracts From Feed Slurry and Filter Cake Produced in Condition 5 of HTI Run PB-04.

FATE OF PS

Earlier work with samples from Runs POC-2, CMSL-8, and CMSL-9, in which virgin polystyrene was a feedstock, indicated that ~70% of the PS fed could be identified as components (toluene, ethylbenzene, and cumene) in the unhydrotreated product oil and ~50% in the hydrotreated product oil.¹⁻⁴ Cumene alone accounted for ~16% of the PS fed in the unhydrotreated product oil, and ~10% in the hydrotreated product oil. Cumene is a good marker for PS-derived products, because it is found in product oil samples from co-liquefaction with PS as a feed component. In the unhydrotreated first-stage product oils from Run PB-04, 1,3-dimethyl propane was also identified as a unique PS marker. However, this compound seems to be clearly identifiable and quantifiable primarily when the product oil is unhydrotreated. The components used for identification and quantification by CONSOL contain aromatic rings, because these components are readily identified by their mass spectra using automated searches of spectral databases.

Concentrations of four PS-derived compounds identified by GC-MS in the SOH1 samples from Run PB-04 and in the Run CMSL-11 product oil from Condition 3B are shown in Table 4. The presence of cumene in products from liquefaction of MSW in Run CMSL-11 and ASR in Run PB-04 demonstrates the presence of PS as a feed component. The ASR and MSW feed materials are very heterogeneous and are difficult to characterize directly to quantify individual polymer components. Based on earlier work with virgin plastics, the amount of PS in the waste feedstocks can be estimated for Runs CMSL-11 and PB-04. If the same degree of conversion takes place, and the yield of the product oils are known or estimated, it is estimated that PS constitutes about 2 wt % of the MF feed MSW in Condition 3B of Run CMSL-11. Similarly, it is estimated that PS constitutes about 12 wt % of the MF feed ASR in Conditions 3 and 4 of Run PB-04.

Table 3. Overall conversion of Feed and Polymer Feed Components in HTI Runs PB-04 and CMSL-11

Source	Overall Conversion, %					
	PB-04 Cond. 1	PB-04 Cond. 2	PB-04 Cond. 3	PB-04 Cond. 4	PB-04 Cond. 5	CMSL-11 Cond. 3B
Basis: MAF Fresh Feed, Ash-Balanced						
CONSOL	93.7	95.0	95.7	87.1	85.5	94.3
HTI(a)	93.2	96.4	94.1	90.5	91.3	94.7
Basis: MAF Fresh Waste/Polymer, Ash-Balanced						
CONSOL	NA	99.9(b)	99.4(b)	95.8(b)	96.8(b)	99.1(c)
Basis: Fresh Decalin-Extractable Polyolefins in Feed, Ash-Balanced						
CONSOL	NA	NA	99.3(c,d)	95.4(c,d)	NA	NA

(a) SO₃-free ash basis

(b) % MAF ASR in feed (+ virgin polymers in feed in Condition 5)

(c) % Decalin-extracted polyolefin in feed (d) Back-calculation from Condition 3 results indicates that the feed ASR contains 79% MAF decalin-extracted polyolefin (63% on MF basis). From Condition 4 results, the feed ASR contains 90% MAF decalin-extracted polyolefin (72% on MF basis).

The four marker compounds (Table 4, Figure 2) constituted about 11-42% of the SOH1 samples in Conditions 3-5 of Run PB-04. In contrast, the Condition 1 (coal-only) SOH1 contained only 2% of three of these markers (1,3 diphenyl propane was not present). In general, these marker compounds seem to represent the lowest-boiling primary fragments of PS liquefaction, as shown in Figure 1. Benzene, methane, and ethane could also be primary products, but they also are produced from coal. Hydrotreating these components may cause cracking or ring hydrogenation. Any products that elute before toluene, or do not contain an aromatic ring, are less-readily identified or quantified because they are not unique to PS liquefaction.

The observed distributions of these four components on relative weight percent and mol percent bases are given in Table 4. An uneven distribution of alkyl/aryl phenyl groups in the products (ethylbenzene has the proper distribution) would imply that these products are accompanied by the production of some (unobserved) combination of methane, ethane, benzene, and cyclohexane (in the simplest possible molecules). The observed distribution indicates that 3.2 mol % benzene + 3.2 mol % methane would account for the imbalance (i.e., there is more cumene than toluene plus 1,3-diphenylpropane). Although the data may not support a rigorous analysis like this, qualitatively the results suggest that the production of light gases such as methane and ethane from liquefaction of polystyrene is minor. These estimates leave about 20% of the PS as unaccounted. In addition to benzene, the unaccounted portion could be cyclic alkyls that are hydrogenation products and not readily identified.

PRIMARY POLYSTYRENE PRODUCTS FOUND BY GC-MS

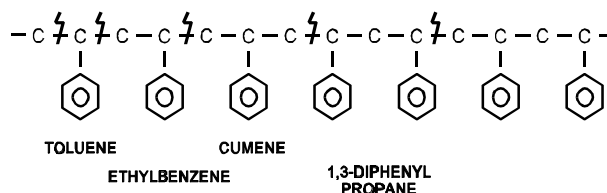


Figure 2. PS Liquefaction Products Found in Net Product Oils.

Table 4. PS Liquefaction Products Found in Run PB-04 First-Stage Oils

Component	Toluene	Ethylbenzene	Cumene	1,3-Diphenyl propane	Sum
Conc. in SOH1, wt %					
Condition 1	0.3	1.7	0.2	0.0	2.2
Condition 3	1.3	7.5	1.9	0.2	10.8
Condition 4	4.0	15.8	5.1	0.6	25.5
Condition 5	4.4	26.8	9.4	1.0	41.6
Conc. in SOH1 as wt % of ASR fed, adjusted to eliminate coal contribution					
Condition 3	1.4	8.0	2.1	0.2	11.7
Condition 4	1.1	4.2	1.6	0.2	7.1
Condition 5	3.0	18.2	6.6	0.7	28.5
Avg. Relative Distribution					
wt %	12.6 ±2.7	63.7 ±4.9	21.4 ±2.8	2.4 ±0.5	100.0
mol%	14.7	64.8	19.2	1.3	100.0
C Balance	+1CH ₂	0	-1CH ₂	+1CH ₂	
Net C Balance	-3.2 mol% CH ₂ , or +3.2 mol% (benzene +CH ₂)				

CONCLUSIONS AND FUTURE NEEDS

These results show that several components of authentic waste polymers can be identified and sometimes quantified in co-liquefaction process stream samples. Different characterization strategies are needed to accommodate different polymers. PS and PP appear to be reactive, and there is no hint that the ASR contains an unreactive PS component, as was speculated based on Run PB-04. HDPE is less reactive and requires a substantial recycle rate to convert it. Ultimately, nearly all of the HDPE is converted. Marker compounds that appear to be primary PS products were observed in the light product range. The distribution of these light PS products suggests that little gas production is associated with PS liquefaction.

It is desirable to develop methods for speciation of more polymers (e.g., polyurethane). Quantitative FTIR methods would allow the determination of relative or absolute amounts of PP and HDPE present. Other information, such as molecular weight distributions, would be informative; however, their expense usually cannot be justified for a large number of process samples.

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